

## Supporting Information

### Probing the effect of heterocycle-bonding in PNX-type ruthenium pre-catalysts for reactions involving H<sub>2</sub>

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1. Experimental Details
2. NMR spectra
3. X-Ray crystal structure determination
4. Literature

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## 1. Experimental Details

**General:** Unless mentioned otherwise, all experiments were carried out under purified Ar or N<sub>2</sub> atmosphere, using standard Schlenk-techniques. All solvents were dried and freshly distilled prior to use. THF was dried with Na/K alloy, CH<sub>2</sub>Cl<sub>2</sub> was dried with CaH<sub>2</sub>, toluene and benzene were dried with sodium and EtOH was dried over magnesium. C<sub>6</sub>D<sub>6</sub> was distilled from Na/K and stored over molecular sieves. All other deuterated solvents were sparged with argon and stored over molecular sieves. [(Ph<sub>3</sub>P)<sub>3</sub>RuCl<sub>2</sub>]<sup>1</sup>, [(Ph<sub>3</sub>P)<sub>3</sub>Ru(H)(Cl)(CO)]<sup>2</sup>, 2-(diphenylphosphino)ethylamine<sup>3</sup> and L<sub>1</sub><sup>3</sup> were prepared according to previously reported procedures. 2-picolyl aldehyde, 2-furaldehyde, thiophen-2-carboxaldehyd, pyrrole-2-carboxaldehyde, RuCl<sub>3</sub>·3H<sub>2</sub>O, PPh<sub>3</sub> and NaBH<sub>4</sub> were purchased from Sigma-Aldrich and used as received.

<sup>1</sup>H NMR and <sup>13</sup>C{<sup>1</sup>H} NMR measurements were recorded using a Bruker Avance 300 MHz spectrometer at 25 °C. <sup>31</sup>P{<sup>1</sup>H} NMR measurements were carried out using a DPX 250 MHz spectrometer at 25 °C. <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR chemical shifts are reported in ppm downfield from tetramethylsilane. The resonance of the residual protons in the deuterated solvent was used as internal standard for <sup>1</sup>H NMR spectroscopy. The solvent peak of the deuterated solvent was used as internal standard for <sup>13</sup>C NMR spectroscopy. <sup>31</sup>P NMR chemical shifts are reported in ppm downfield from H<sub>3</sub>PO<sub>4</sub> and referenced to an external 85% solution of phosphoric acid in D<sub>2</sub>O. The following abbreviations are used for the description of NMR data: br (broad), s (singlet), d (doublet), t (triplet), m (multiplet), v (virtual). FT-IR spectra were recorded by attenuated total reflection of the solid samples on a Bruker Tensor IF37 spectrometer. The intensity of the absorption band is indicated as vw (very weak), w (weak), m (medium), s (strong), vs (very strong) and br (broad). HR-ESI and HR-APCI mass spectra were acquired with a LTQ-FT mass spectrometer (Thermo Fisher Scientific). In both cases the resolution was set to 100.000. Elemental analyses were performed on a Vario Micro Cube Elemental Analyzer. Gas chromatography was performed with *m*-xylene as internal standard with an HP-5 column and an Agilent 6850 series GC system.

**Synthesis of 2-(diphenylphosphanyl)-N-(furan-2-ylmethyl)ethaneamine (L<sub>2</sub>):** 2-furaldehyde (106 mg, 1.10 mmol) was slowly added to a solution of 2-(diphenylphosphino)ethylamine (1.00 mmol, 229 mg) in 4 mL of THF and the mixture was stirred for 16 h at ambient temperature. The formation of the corresponding imine was confirmed using <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy ( $\delta$  = -18.14 (s) ppm). After removal of all volatiles, the remaining yellow oil was dissolved in 5 mL of methanol, followed by the addition of NaBH<sub>4</sub> (45 mg, 1.20 mmol). After stirring at ambient temperature for 16 h the solvent was removed *in vacuo* and the residue was extracted with toluene (2×10 mL). After removal of all volatiles and drying under high vacuum the analytical pure product was obtained as a yellow oil. Yield: 266 mg (0.86 mmol, 86.2% based on 2-(diphenylphosphino)ethylamine). Anal. Calcd. for C<sub>19</sub>H<sub>20</sub>NOP (M = 309.34 g/mol) C 73.77%, H, 6.52%, N 4.53%. Found: C 73.81%, H 6.52%, N 4.94%. <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C)  $\delta$ : 1.05 (br, 1H, NH), 2.09 (m, 2H, CH<sub>2</sub>), 2.65 (ddd, *J* = 13.3, *J* = 10.1, *J* = 7.7 Hz, 2H, CH<sub>2</sub>), 3.48 (d, <sup>3</sup>*J*<sub>HH</sub> = 6.9 Hz, 2H, CH<sub>2</sub>), 5.95 (dd, <sup>3</sup>*J*<sub>HH</sub> = 3.1 Hz, <sup>3</sup>*J*<sub>HH</sub> = 0.8 Hz, 1H, furan-H), 6.08 (dd, <sup>3</sup>*J*<sub>HH</sub> = 3.2 Hz, <sup>3</sup>*J*<sub>HH</sub> = 1.9 Hz, 1H, furan-H), 7.05-7.09 (m, 6H, Ph-H), 7.38-7.43 (m, 4H, Ph-H), 7.58 (m, 1H, furan-H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C)  $\delta$ : 29.6 (d, <sup>2</sup>*J*<sub>CP</sub> = 13.0 Hz, 1C, PCH<sub>2</sub>CH<sub>2</sub>), 46.2 (d, <sup>1</sup>*J*<sub>CP</sub> = 20.2 Hz, 1C, PCH<sub>2</sub>), 46.3 (s, 1C, NHCH<sub>2</sub>), 106.6 (s, 1C, furan-C), 110.4 (s, 1C, furan-C), 128.6 (d, <sup>3</sup>*J*<sub>CP</sub> = 6.6 Hz, 4C, *m*-Ph-C), 133.1 (d, <sup>2</sup>*J*<sub>CP</sub> = 18.8 Hz, 4C, *o*-Ph-C), 139.6 (s, 2C, *p*-Ph-C), 139.8 (s, 1C, furan-C), 141.6 (s, 2C, *i*-Ph-C), 155.1 (s, 1C, furan-C) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (101 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C)  $\delta$ : -18.6 (s, 1P) ppm. HR ESI-MS (*m/z*): 310.1355 ([L+H]<sup>+</sup><sub>calc</sub>), 310.1353 (found, 100%). IR (thin film,  $\tilde{\nu}$ /cm<sup>-1</sup>): 3070 (w),

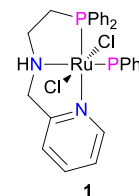
2892 (w), 2344 (w), 1657 (vw), 1592 (m), 1495 (vw), 1422 (m), 1326 (m), 1263 (m), 1202 (m), 1167 (m), 1103 (br), 1012 (s), 909 (m), 786 (s), 740 (vs), 683 (vs), 606 (m), 513 (m).

**Synthesis of 2-(diphenylphosphanyl)-N-(thiophen-2-ylmethyl)ethaneamine (L<sub>3</sub>):** Thiophen-2-carboxaldehyde (123 mg, 1.10 mmol) was slowly added to a solution of 2-(diphenylphosphino)ethylamine (1.00 mmol, 229 mg) in 3.5 mL of THF and the mixture was stirred for 16 h. The formation of the corresponding imine was confirmed using <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy ( $\delta = -16.6$  (s) ppm). After removal of all volatiles, the remaining yellow oil was dissolved in 5 mL of methanol, followed by the addition of NaBH<sub>4</sub> (45 mg, 1.20 mmol). After stirring at ambient temperature for 16 h, the solvent was removed *in vacuo* and the residue was extracted with toluene (2×10 mL). After removal of all volatiles and drying under high vacuum the analytical pure product was obtained as a pale yellow oil. Yield: 207 mg. (0.64 mmol, 63.7% based on 2-(diphenylphosphino)ethylamine). Anal. Calcd. for C<sub>19</sub>H<sub>20</sub>NPS·CH<sub>3</sub>OH (M = 357.13 g/mol) C 67.20%, H 6.77%, N 3.92%. Found: C 66.52%, H 6.32%, N 3.82%. <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C)  $\delta$ : 1.02 (br, 1H, NH), 2.08 (t, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz, 2H, PCH<sub>2</sub>), 2.66 (dt, J = 15.4 Hz, J = 7.8 Hz, 2H, PCH<sub>2</sub>CH<sub>2</sub>), 3.61 (dd, <sup>3</sup>J<sub>HH</sub> = 6.6 Hz, <sup>3</sup>J<sub>HH</sub> = 0.8 Hz, 2H, CH<sub>2</sub>), 6.74 (m, 1H, thiophene-H), 6.85 (dd, <sup>3</sup>J<sub>HH</sub> = 5.0 Hz, <sup>3</sup>J<sub>HH</sub> = 1.3 Hz, 1H, thiophene-H), 6.89 (dd, <sup>3</sup>J<sub>HH</sub> = 5.0 Hz, <sup>3</sup>J<sub>HH</sub> = 1.3 Hz, 1H, thiophene-H), 7.06-7.09 (m, 6H, Ph-H), 7.37-7.44 (m, 4H, Ph-H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C)  $\delta$ : 29.5 (d, <sup>2</sup>J<sub>CP</sub> = 13.1 Hz, 1C, PCH<sub>2</sub>CH<sub>2</sub>), 46.2 (d, <sup>1</sup>J<sub>CP</sub> = 20.9 Hz, 1C, PCH<sub>2</sub>CH<sub>2</sub>), 48.4 (s, 1C, NHCH<sub>2</sub>), 124.2 (s, 1C, thiophene-C), 124.4 (s, 1C, thiophene-C), 126.5 (s, 1C, thiophene-C), 128.3 (s, 2C, p-Ph-C), 128.6 (d, <sup>3</sup>J<sub>CP</sub> = 6.3 Hz, 4C, m-Ph-C), 133.1 (d, <sup>2</sup>J<sub>CP</sub> = 6.6 Hz, 4C, o-Ph-C), 139.5 (d, <sup>1</sup>J<sub>CP</sub> = 14.3 Hz, 2C, i-PPH-C), 145.2 (s, 1C, thiophene-C) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (101 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C)  $\delta$ : -13.6 (s, 1P) ppm. HR ESI-MS (m/z): 326.1126 ([L+H]<sup>+</sup><sub>calc</sub>), 326.1122 (found, 100%). IR (thin film,  $\tilde{\nu}/\text{cm}^{-1}$ ): 3070 (w), 2907 (vw), 2843 (w), 2397 (vw), 2377 (w), 1577 (w), 1422 (m), 1365 (m), 1307 (w), 1268 (vw), 1217 (m), 1183 (m), 1153 (m), 1058 (s), 1028 (s), 956 (s), 854 (m), 825 (m), 730 (m), 683 (vs), 546 (vw), 510 (m), 498 (m), 450 (w), 411 (vw).

**Synthesis of 2-(diphenylphosphanyl)-N-(1H-pyrrol-2-ylmethyl)ethaneamine (L<sub>4</sub>):** Pyrrole-2-carboxaldehyde (104 mg, 1.10 mmol) was slowly added to a solution of 2-(diphenylphosphino)ethylamine (1.00 mmol, 2.30 mL, 229 mg) in 5 mL of THF and the mixture was stirred at 40 °C for 16 h, resulting in the formation of a white precipitate. The precipitate was identified as the pure imine by <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy ( $\delta = -12.84$  (s) ppm), but the supernatant solution still contained imine. After removal of the THF, the residue was washed with ethanol (2×3 mL), n-hexane (2×3 mL) and dried under vacuum for 2 h. The white solid was suspended in 5 mL methanol and NaBH<sub>4</sub> (45 mg, 1.20 mmol) was added to the suspension. After stirring at ambient temperature for 16 h the solvent was removed *in vacuo* and the residue was extracted with toluene (2×10 mL). After the solvent evaporation, the product was dried under vacuum for 3 h to give the product as pale white solid. Yield: 157 mg (0.51 mmol, 50.9% based on 2-(diphenylphosphino)ethylamine). Anal. Calcd. for C<sub>19</sub>H<sub>21</sub>N<sub>2</sub>P·C<sub>7</sub>H<sub>8</sub> (M = 400.20 g/mol) C 77.97%, N 6.99%, H 7.30%. Found: C 77.99%, N 6.98%, H 7.16%. <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C)  $\delta$ : 0.78 (br, 1H, NH), 2.04 (t, J = 7.3 Hz, 2H, PCH<sub>2</sub>), 2.59 (dd, <sup>2</sup>J<sub>HH</sub> = 16.6 Hz, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz, 2H, PCH<sub>2</sub>CH<sub>2</sub>), 3.41 (s, 2H, CH<sub>2</sub>), 6.10 (s, 1H, pyrrole-NH), 6.29 (d, <sup>3</sup>J<sub>HH</sub> = 2.7 Hz, 1H, pyrrole-H), 6.44 (m, 1H, pyrrole-H), 7.08-7.06 (m, 7H, Ph-H+pyrrole-H), 7.42 (s, 4H, Ph-H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C)  $\delta$ : 29.7 (d, <sup>2</sup>J<sub>CP</sub> = 12.8 Hz, 1C, PCH<sub>2</sub>CH<sub>2</sub>), 46.2 (d, <sup>1</sup>J<sub>CP</sub> = 19.7 Hz, 1C, PCH<sub>2</sub>CH<sub>2</sub>), 46.5 (s, 1C, NHCH<sub>2</sub>), 106.1 (s, 1C, pyrrole-C), 108.4 (s, 1C, pyrrole-C), 116.8 (s, 1C, pyrrole-C), 128.7 (s, 3C, p-Ph-C+pyrrole-C), 128.8 (d, <sup>3</sup>J<sub>CP</sub> = 6.4 Hz, 4C, m-Ph-C), 133.1 (d, <sup>2</sup>J<sub>CP</sub> = 18.9 Hz, 4C, o-Ph-C) ppm,

139.9 (s, 2C, *i-Ph-C*).  $^{31}\text{P}\{^1\text{H}\}$  NMR (101 MHz,  $\text{C}_6\text{D}_6$ , 25 °C)  $\delta$ : -17.8 (s, 1P) ppm. HR ESI-MS ( $m/z$ ): 309.1515 ( $[\text{L}+\text{H}]^+$  calc), 309.1510 (found, 100%). IR (thin film,  $\tilde{\nu}/\text{cm}^{-1}$ ): 3262 (w), 3233 (vw), 3162 (w), 3082 (w), 2965 (w), 2879 (w), 2852 (w), 2354 (w), 1954 (vw), 1592 (w), 1475 (w), 1422 (m), 1333 (w), 1251 (m), 1103 (s), 978 (s), 919 (w), 848 (w), 808 (s), 717 (s), 683 (vs), 586 (w), 513 (s), 505 (s), 445 (m), 399 (m).

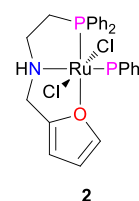
**Synthesis of  $[(\text{L}_1)\text{RuCl}_2(\text{PPh}_3)]$  (**1**):** This complex was synthesized according to a previously reported procedure.<sup>3</sup>  $\text{L}_1$  (16 mg, 0.050 mmol) and  $[(\text{PPh}_3)_3\text{RuCl}_2]$  (48 mg, 0.050 mmol) were dissolved in 15 mL dichloromethane and stirred at room temperature for 3 h, yielding a yellow solution. After removal of dichloromethane, the residue was washed with diethyl ether. And dried under a high vacuum for 3 h to give pure **1**. Single crystals, suitable for single crystal X-ray diffraction were



grown by layering a concentrated dichloromethane solution with diethyl ether. Yield: 34 mg (0.045 mmol, 90.0%). Anal. Calcd. for  $\text{C}_{38}\text{H}_{36}\text{Cl}_2\text{N}_2\text{P}_2\text{Ru}_1 \cdot \text{CH}_2\text{Cl}_2$  ( $M = 838.03$  g/mol) C 55.79%, N 3.34%, H 4.56%, Found: C 55.49%, N 3.58%, H 4.34%.  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_2\text{Cl}_2$ , 25 °C)  $\delta$ : 2.75 (m, 2H,  $\text{CH}_2$ ), 3.46 (m, 2 H,  $\text{CH}_2$ ), 4.28 (m, 1H,  $\text{CH}_2$ ), 5.24 (br, 1H, NH), 5.52 (t,  $^2J_{\text{HH}} = 13.1$  Hz, 1H,  $\text{CH}_2$ ), 6.89 (t,  $^3J_{\text{HH}} = 6.6$  Hz, 1H, *Py-H*), 7.20 (m, 24H, *Ph-H+Py-H*), 7.67 (m, 3H, *Ph-H+Py-H*), 8.46 (d,  $^3J_{\text{HH}} = 4.8$  Hz, 1H, *Py-H*) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CD}_2\text{Cl}_2$ , 25 °C)  $\delta$ : 39.6 (s, 1C,  $\text{CH}_2$ ), 48.9 (s, 1C,  $\text{CH}_2$ ), 57.7 (s, 1C,  $\text{CH}_2$ ), 121.8 (s, 1C, *Py-C*), 122.6 (s, 1C, *Py*), 127.5 (m, 10C, *Ph-C*), 129.2 (d,  $^4J_{\text{CP}} = 2.3$  Hz, 2C, *p-Ph-C*), 129.3 (d,  $^4J_{\text{CP}} = 2.3$  Hz, 3C, *p-Ph-C*), 134.4 (d,  $^2J_{\text{CP}} = 9.8$  Hz, 2C, *o-Ph-C*), 135.0 (d,  $^2J_{\text{CP}} = 9.0$  Hz, 2C, *o-Ph-C*), 135.4 (d,  $^2J_{\text{CP}} = 9.7$  Hz, 6C, *o-Ph-C*), 136.7 (s, 3C, *i-Ph-C*), 137.3 (s, 1C, *Py-C*), 137.8 (s, 2C, *i-PPH\_2-C*), 156.7 (s, 1C, *Py-C*), 163.5 (s, 1C, *Py-C*) ppm.  $^{31}\text{P}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CD}_2\text{Cl}_2$ , 25 °C)  $\delta$ : 47.3 (d,  $^2J_{\text{PP}} = 29.0$  Hz, 1P), 49.1 (d,  $^2J_{\text{PP}} = 28.9$  Hz, 1P) ppm.

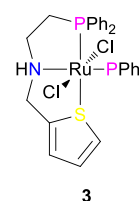
HR ESI-MS ( $m/z$ ): 719.1087 ( $[\text{M}-\text{Cl}]^+$  calc), 719.1085 (found, 100%). IR (thin film,  $\tilde{\nu}/\text{cm}^{-1}$ ): 3165 (vw), 3048 (w), 2931 (vw), 2325 (vw), 1582 (w), 1497 (m), 1443 (m), 1093 (m), 965 (m), 883 (vw), 817 (m), 710 (vs), 562 (m), 533 (m), 509 (s), 424 (m).

**Synthesis of  $[(\text{L}_2)\text{RuCl}_2(\text{PPh}_3)]$  (**2**):** Ligand  $\text{L}_2$  (16 mg, 0.050 mmol) and  $[(\text{PPh}_3)_3\text{RuCl}_2]$  (48 mg, 0.050 mmol) dissolved in 15 mL of toluene were heated to 100 °C for 16 h, resulting in a dark red solution. After removal of the toluene the residue was washed with *n*-hexane and dried under high vacuum to give pure **2**. Single crystals, suitable for single crystal X-ray diffraction analysis were grown by layering a concentrated toluene/ $\text{CH}_2\text{Cl}_2$  solution with *n*-hexane. Yield: 32 mg (0.043 mmol, 86.1%). Anal. Calcd. for  $\text{C}_{37}\text{H}_{35}\text{Cl}_2\text{N}_1\text{O}_1\text{P}_2\text{Ru}_1 \cdot 0.25\text{CH}_2\text{Cl}_2$  ( $M = 764.83$  g/mol) C 58.50%, N 1.83%, H 4.68%. Found: C 58.58%, N 1.83%, H 4.26%.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 25 °C)  $\delta$ : 2.54 (m, 1H,  $\text{CH}_2$ ), 2.71 (vt,  $J = 15.0$  Hz, 1H,  $\text{CH}_2$ ), 3.39 (m, 2H,  $\text{CH}_2$ ), 3.95 (dt,  $^2J_{\text{HH}} = 12.9$  Hz,  $J = 3.0$  Hz, 1H,  $\text{CH}_2$ ), 4.82 (vt,  $J = 12.0$  Hz, 1H,  $\text{CH}_2$ ), 4.99 (br, 1H, NH), 5.88 (m, 1H, *furan-H*), 5.95 (m, 1H, *furan-H*), 6.10 (d,  $^3J_{\text{HH}} = 3.0$  Hz, 1H, *furan-H*), 6.78-6.96 (m, 4H, *PPh\_2-H*), 6.97-7.11 (m, 8C, *PPh\_3+PPh\_2-H*), 7.18-7.29 (m, 7H, *PPh\_3+PPh\_2-H*), 7.38-7.45 (vt,  $J = 8.4$  Hz, 6H, *PPh\_3-H*) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ , 25 °C)  $\delta$ : 43.1 (s, 1C,  $\text{CH}_2$ ), 47.7 (s, 1C,  $\text{CH}_2$ ), 48.2 (s, 1C,  $\text{CH}_2$ ), 108.7 (s, 1C, *furan-C*), 109.5 (s, 1C, *furan-C*), 110.3 (s, 1C, *furan-C*), 127.5 (m, 4C, *m-Ph-C*), 127.7 (d,  $^3J_{\text{CP}} = 9.2$  Hz, 6C, *m-Ph-C*), 129.1 (d,  $^4J_{\text{CP}} = 2.3$  Hz, 5C, *p-Ph-C*), 133.6 (d,  $^2J_{\text{CP}} = 9.5$  Hz, 4C, *o-Ph-C*), 134.2 (d,  $^2J_{\text{CP}} = 9.5$  Hz, 6C, *o-Ph-C*), 134.9 (s, 3C, *i-Ph-C*), 135.0 (s, 2C, *i-Ph-C*), 142.8 (s, 1C, *i-furan-C*) ppm.  $^{31}\text{P}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ , 25 °C)  $\delta$ : 81.5 (d,  $^2J_{\text{PP}} = 33.1$  Hz, 1P); 54.0 (d,  $^2J_{\text{PP}} = 37.3$  Hz, 1P) ppm. HR ESI-MS ( $m/z$ ): 1453.1549 ( $[2\text{M}-\text{Cl}]^+$  calc), 1453.1554 (found, 40%); 1191.0630 ( $[2\text{M}-\text{Cl}-\text{PPh}_3]^+$  calc), 1191.0636 (found, 40%); 928.9711 ( $[2\text{M}-\text{Cl}-\text{PPh}_3]_2^+$  calc), 928.9717 (found, 16%). IR (thin film,  $\tilde{\nu}/\text{cm}^{-1}$ ): 3170



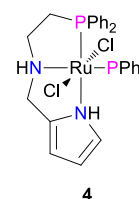
(w), 3134 (vw), 3050 (w), 2914 (w), 2926 (w), 2667 (w), 2349 (w), 2326 (w), 1480 (w), 1437 (m), 1255 (m), 1190 (w), 1134 (w), 1074 (m), 996 (m), 907 (m), 900 (m), 823 (m), 739 (s), 684 (s), 661 (m), 520 (s), 421 (w), 415 (m).

**Synthesis of [(L<sub>3</sub>)RuCl<sub>2</sub>(PPh<sub>3</sub>)] (3):** Ligand L<sub>3</sub> (16 mg, 0.050 mmol) and [(PPh<sub>3</sub>)<sub>3</sub>RuCl<sub>2</sub>] (48 mg, 0.050 mmol) were dissolved in 15 mL of toluene and heated to 100 °C for 16 h, resulting in a dark red solution. After removal of the toluene, the residue was washed with *n*-hexane and dried under high vacuum, to give pure **3**. Single crystals, suitable for single crystal X-ray diffraction analysis were grown by layering a concentrated toluene solution with *n*-hexane. Yield: 32 mg (0.042 mmol,



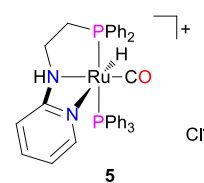
84.2%). Anal. Calcd. for C<sub>37</sub>H<sub>35</sub>Cl<sub>2</sub>N<sub>1</sub>P<sub>2</sub>S<sub>1</sub>Ru<sub>1</sub>·1.5toluene (M = 897.12 g/mol) C 63.54%, N 1.56%, H 5.28%. Found: C 63.79%, N 1.74%, H 5.65%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C) δ: 2.33 (m, 1H, CH<sub>2</sub>), 2.76 (t, *J* = 15.3 Hz, 1H, CH<sub>2</sub>), 3.40 (m, 1H, CH<sub>2</sub>), 3.95 (d, <sup>2</sup>*J*<sub>HH</sub> = 11.4 Hz, 1H, CH<sub>2</sub>), 4.47 (m, 2H, CH<sub>2</sub>), 4.59 (br, 1H, NH), 5.78 (d, <sup>3</sup>*J*<sub>HH</sub> = 5.1 Hz, 1H, thiophene-H), 6.76-6.92 (m, 2H, thiophene-H), 6.92-7.04 (m, 4H, PPh<sub>2</sub>-H), 7.09-7.40 (m, 15H, Ph-H), 7.52 (vt, *J* = 8.7 Hz, 6H, PPh<sub>3</sub>-H) ppm. <sup>13</sup>C{<sup>1</sup>H}NMR (75 MHz, CDCl<sub>3</sub>, 25 °C) δ: 48.9 (s, 2C, CH<sub>2</sub>), 49.4 (s, 1C, CH<sub>2</sub>), 100.2 (s, 2C, thiophene-C), 126.6 (s, 1C, thiophene-C), 127.6 (m, 10C, *m*-Ph-C), 128.8 (d, <sup>4</sup>*J*<sub>CP</sub> = 2.2 Hz, 2C, *p*-Ph-C), 133.9 (d, <sup>4</sup>*J*<sub>CP</sub> = 2.3 Hz, 3C, *p*-Ph-C), 134.91 (d, <sup>3</sup>*J*<sub>CP</sub> = 9.8 Hz, 10C, *o*-Ph-C), 138.1 (s, 5C, *i*-Ph-C), 138.7 (s, 1C, thiophene-C) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>, 25 °C) δ: 63.2 (d, <sup>2</sup>*J*<sub>PP</sub> = 37.3 Hz, 1P), 45.2 (d, <sup>2</sup>*J*<sub>PP</sub> = 35.4 Hz, 1P) ppm. HR ESI-MS (*m/z*): 724.0698 ([M-Cl]<sup>+</sup><sub>calc</sub>), 724.0647 (found, 70%). IR (thin film,  $\tilde{\nu}$ /cm<sup>-1</sup>): 3174 (w), 3037 (vw), 2953 (w), 2899 (w), 2825 (w), 1577 (w), 1482 (w), 1472 (w), 1432 (m), 1377 (w), 1273 (s), 1249 (w), 1090 (s), 1012 (s), 943 (m), 89 (w), 787 (s), 727 (m), 692 (s), 647 (w), 594 (w), 493 (s), 485 (m), 436 (w), 380 (m).

**Synthesis of [(L<sub>4</sub>)RuCl<sub>2</sub>(PPh<sub>3</sub>)] (4):** Ligand L<sub>4</sub> (16 mg, 0.050 mmol) and (PPh<sub>3</sub>)<sub>3</sub>RuCl<sub>2</sub> (48 mg, 0.050 mmol) were dissolved in 15 mL of CH<sub>2</sub>Cl<sub>2</sub> and stirred at ambient temperature for 16 h, resulting in a yellow solution. After removal of CH<sub>2</sub>Cl<sub>2</sub>, the precipitate was washed with diethyl ether and dried under high vacuum, to give pure **4**. Single crystals suitable for single crystal X-ray diffraction analysis were grown by layering a concentrated toluene solution with diethyl ether. Yield: 36 mg



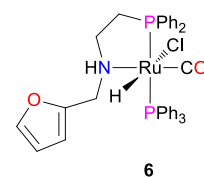
(0.048 mmol, 97.0%). Anal. Calcd. for C<sub>37</sub>H<sub>36</sub>Cl<sub>2</sub>N<sub>2</sub>P<sub>2</sub>Ru<sub>1</sub>·0.5CH<sub>2</sub>Cl<sub>2</sub> (M = 785.02 g/mol) C 57.37%, N 3.57%, H 4.75%, Found: C 57.85%, N 3.73%, H 4.92%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C) δ: 2.90 (m, 1H, CH<sub>2</sub>), 3.14 (vt, *J* = 11.3 Hz, 1H, CH<sub>2</sub>), 3.58 (d, <sup>3</sup>*J*<sub>HH</sub> = 6.9 Hz, 1H, CH<sub>2</sub>), 3.91 (dd, *J*<sub>HH</sub> = 22.2 Hz, *J*<sub>HH</sub> = 4.2 Hz, 1H, CH<sub>2</sub>), 4.14 (br, 1H, NH), 4.36 (m, 1H, CH<sub>2</sub>), 4.99 (m, 1H, CH<sub>2</sub>), 5.61 (br, 1H, pyrrole-NH), 6.79 (d, <sup>3</sup>*J*<sub>HH</sub> = 5.4 Hz, 1H, pyrrole-H), 7.19-7.28 (m, 1H, pyrrole-H), 7.28-7.60 (m, 16H, Ph-H), 7.52 (vt, *J* = 8.1 Hz, 3H, PPh<sub>3</sub>-H), 7.77 (vt, *J* = 8.1 Hz, 6H, PPh<sub>3</sub>-H), 8.08 (m, 1H, pyrrole-H) ppm. <sup>13</sup>C{<sup>1</sup>H}NMR (75 MHz, CDCl<sub>3</sub>, 25 °C) δ: 49.1 (s, 1C, CH<sub>2</sub>), 52.6 (s, 1C, CH<sub>2</sub>), 68.8 (s, 1C, CH<sub>2</sub>), 127.1 (d, <sup>2</sup>*J*<sub>CP</sub> = 2.8 Hz, 1C, pyrrole-C), 127.2-127.5 (m, 12C, pyrrole + *m*-Ph-C), 128.7 (d, <sup>4</sup>*J*<sub>CP</sub> = 1.9 Hz, 3C, *p*-Ph-C), 129.1 (d, <sup>4</sup>*J*<sub>CP</sub> = 1.9 Hz, 1C, *p*-Ph-C), 129.1 (d, <sup>4</sup>*J*<sub>CP</sub> = 1.9 Hz, 1C, *p*-Ph-C), 134.2 (dd, <sup>2</sup>*J*<sub>CP</sub> = 8.8, <sup>2</sup>*J*<sub>CP</sub> = 4.4 Hz, 4C, *o*-Ph-C), 135.1 (d, <sup>2</sup>*J*<sub>CP</sub> = 9.8 Hz, 6C, *o*-Ph-C), 137.6 (s, 2C, *i*-Ph-C), 138.1 (s, 3C, *i*-Ph-C) 153.1 (s, 1C, pyrrole-C) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>, 25 °C) δ: 50.9 (d, <sup>2</sup>*J*<sub>PP</sub> = 30.3 Hz, 1P), 50.0 (d, <sup>2</sup>*J*<sub>PP</sub> = 30.6 Hz, 1P) ppm. HR ESI-MS (*m/z*): 707.1087 ([M-Cl]<sup>+</sup><sub>calc</sub>), 707.1077 (found, 55%). IR (thin film,  $\tilde{\nu}$ /cm<sup>-1</sup>): 3055 (w), 3043 (w), 1602 (w), 1586 (vw), 1500 (w), 1431 (m), 1277 (w), 1192 (w), 1203 (w), 1096 (m), 1079 (m), 1011 (m), 958 (w), 818 (m), 738 (m), 681 (s), 628 (w), 534 (s), 428 (w), 399 (m).

**Synthesis of  $[(\kappa^3\text{-L}_1)\text{Ru}(\text{H})(\text{CO})(\text{PPh}_3)]\text{Cl}$  (5):** Ligand  $\text{L}_1$  (16 mg, 0.050 mmol) and  $[(\text{PPh}_3)_3\text{Ru}(\text{H})\text{Cl}(\text{CO})]$  (47 mg, 0.050 mmol) were dissolved in 15 mL of toluene and heated to reflux for 16 h, resulting in a yellow solution. After cooling to room temperature, all volatiles were removed under vacuum and the white residue was washed with diethyl ether three times. Drying under



high vacuum yields pure complex **5**. Single crystals suitable for single crystal X-ray diffraction analysis were grown by layering a concentrated dichloromethane solution with diethyl ether. Yield: 14 mg (0.018 mmol, 37.4%). Anal. Calcd. for  $\text{C}_{39}\text{H}_{37}\text{ClN}_2\text{O}_1\text{P}_2\text{Ru}_1 \cdot 2\text{CH}_2\text{Cl}_2$  ( $M = 918.01$  g/mol) C 53.64%, N 3.05%, H 4.50%, Found: C 53.75%, N 3.34%, H 4.27%.  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_2\text{Cl}_2$ , 25 °C)  $\delta$ : -11.96 (dd,  $^2J_{\text{PH}} = 21.3$ ,  $^2J_{\text{PH}} = 18.5$ , 1H, Ru-H), 1.98 (m, 1H,  $\text{PCH}_2\text{CH}_2$ ), 2.73 (m, 2H,  $\text{PyCH}_2$ ), 3.59 (dd,  $^2J_{\text{HH}} = 16.0$  Hz,  $J = 3.6$  Hz, 1 H,  $\text{PCH}_2\text{CH}_2$ ), 3.68 (br, 1H, NH), 3.90 (d,  $^2J_{\text{HH}} = 15.7$  Hz, 2H,  $\text{PCH}_2\text{CH}_2$ ), 6.50 (vt,  $J = 6.6$  Hz, 1H,  $\text{Py-H}$ ), 6.92 (d, 1H,  $^3J_{\text{HH}} = 7.7$  Hz,  $\text{Py-H}$ ), 7.25-7.36 (m, 16H,  $\text{Ph-H}$ ), 7.47 (m, 3H,  $\text{Ph-H}$ ), 7.52 (d,  $^3J_{\text{HH}} = 5.3$  Hz, 1H,  $\text{Py-H}$ ), 7.61-7.68 (m, 6H,  $\text{Ph-H}$ ), 7.88 (m, 1H,  $\text{Py-H}$ ) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CD}_2\text{Cl}_2$ , 25 °C)  $\delta$ : 31.3 (d,  $^1J_{\text{CP}} = 25.3$  Hz, 1C,  $\text{CH}_2$ ), 51.6 (s, 1C,  $\text{CH}_2$ ), 59.9 (s, 1C,  $\text{CH}_2$ ), 122.3 (s, 1C,  $\text{Py-C}$ ), 123.5 (s, 1C,  $\text{Py-C}$ ), 127.4 (vt,  $J = 4.7$  Hz, 4C,  $m\text{-Ph-C}$ ), 128.6-129.0 (m, 6C,  $m\text{-Ph-C}$ ), 129.9 (d,  $J = 1.9$  Hz, 2C,  $p\text{-Ph-C}$ ), 130.7 (m, 3C,  $p\text{-Ph-C}$ ), 133.0 (d,  $^2J_{\text{CP}} = 11.6$  Hz, 6C,  $o\text{-Ph-C}$ ), 133.4 (d,  $^2J_{\text{CP}} = 12.1$  Hz, 4C,  $o\text{-Ph-C}$ ), 134.1 (d,  $^4J_{\text{CP}} = 1.9$  Hz, 3C,  $i\text{-Ph-C}$ ), 134.5 (vt,  $J = 5.6$  Hz, 2C,  $i\text{-Ph-C}$ ), 136.5 (s, 1C,  $\text{Py-C}$ ), 152.4 (s, 1C,  $\text{Py-C}$ ), 157.2 (s, 1C,  $\text{Py-C}$ ), 203.8 (vt,  $J = 14.5$  Hz, 1C, CO) ppm.  $^{31}\text{P}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CD}_2\text{Cl}_2$ , 25 °C)  $\delta$ : 65.3 (d,  $^2J_{\text{PP}} = 260.6$  Hz, 1P), 45.9 (d,  $^2J_{\text{PP}} = 260.5$  Hz, 1H) ppm. HR ESI-MS ( $m/z$ ): 713.1429 ( $[\text{M-Cl}]^+$  calc), 713.1451 (found, 100%). IR (thin film,  $\tilde{\nu}/\text{cm}^{-1}$ ): 2962 (w), 2360 (vw), 2341 (w), 1920 (m,  $\nu_{\text{CO}}$ ), 1479 (m), 1259 (s), 1089 (s), 1014 (s), 794 (s), 743 (w), 693 (s), 509 (s).

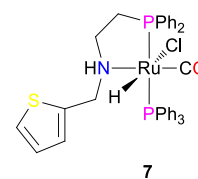
**Synthesis of  $[(\kappa^2\text{-L}_2)\text{Ru}(\text{H})(\text{Cl})(\text{CO})(\text{PPh}_3)]$  (6):** Ligand  $\text{L}_2$  (16 mg, 0.050 mmol) and  $[(\text{PPh}_3)_3\text{Ru}(\text{H})(\text{Cl})(\text{CO})]$  (47 mg, 0.050 mmol) were dissolved in 15 mL of toluene and heated to 100 °C for 3 h, resulting in a yellow solution. After removal of the toluene, the precipitate was washed with *n*-hexane and dried under high vacuum, to give pure **6**. Single crystals suitable for single crystal



X-ray diffraction analysis were grown by layering a concentrated toluene solution with *n*-hexane. Yield: 29 mg (0.039 mmol, 78.6%). Anal. Calcd. for  $\text{C}_{38}\text{H}_{36}\text{Cl}_1\text{N}_1\text{O}_2\text{P}_2\text{Ru}_1 \cdot 2\text{C}_7\text{H}_8$  ( $M = 922.2$  g/mol) C 67.78%, N 1.52%, H 5.69%. Found: C 67.39%, N 1.64%, H 5.75%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25 °C)  $\delta$ : -13.53 (dd,  $^2J_{\text{PH}} = 15.6$  Hz,  $^2J_{\text{PH}} = 8.4$  Hz, 1H, Ru-H), 2.45 (d,  $^3J_{\text{HH}} = 9.90$  Hz, 1H,  $\text{CH}_2$ ), 2.56 (t,  $^3J_{\text{HH}} = 8.40$  Hz, 1H,  $\text{CH}_2$ ), 3.37 (br, 1H, NH), 3.42 (m, 2H,  $\text{CH}_2$ ), 3.63 (m, 2H,  $\text{CH}_2$ ), 5.46 (d,  $^3J_{\text{HH}} = 3.1$  Hz, 1H, furan-H), 6.00 (dd,  $^3J_{\text{HH}} = 3.2$  Hz,  $^3J_{\text{HH}} = 1.9$  Hz, 1H, furan-H), 6.95 (m, 1H, furan-H), 7.07-7.25 (m, 15H,  $\text{Ph-H}$ ), 7.99 (m, 2H,  $\text{Ph-H}$ ), 8.09 (dd,  $J_{\text{HH}} = 10.6$  Hz,  $J_{\text{HH}} = 7.1$  Hz, 2H,  $\text{Ph-H}$ ), 8.24 (m, 6H,  $\text{Ph-H}$ ) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{C}_6\text{D}_6$ , 25 °C)  $\delta$ : 30.0 (s, 2C,  $\text{CH}_2$ ), 50.3 (s, 1C,  $\text{CH}_2$ ), 109.0 (s, 1C, furan-C), 110.4 (s, 1C, furan-C), 128.4-127.3 (m, 10C,  $m\text{-Ph-C}$ ), 129.6 (s, 2C,  $p\text{-Ph-C}$ ), 130.0 (s, 3C,  $p\text{-Ph-C}$ ), 133.3 (d,  $^2J_{\text{CP}} = 7.5$  Hz, 2C,  $o\text{-Ph-C}$ ), 133.7 (d,  $^2J_{\text{CP}} = 10.1$  Hz, 2C,  $o\text{-Ph-C}$ ), 134.6 (d,  $^2J_{\text{CP}} = 10.9$  Hz, 6C,  $o\text{-Ph-C}$ ), 135.5 (s, 2C,  $i\text{-Ph-C}$ ), 135.9 (s, 3C,  $i\text{-Ph-C}$ ), 142.1 (s, 1C, furan-C), 152.0 (s, 1C, furan-C), 203.7 (s, 1C, CO) ppm.  $^{31}\text{P}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ , 25 °C)  $\delta$ : 63.6 (d,  $^2J_{\text{PP}} = 288.0$  Hz, 1P), 49.16 (d,  $^2J_{\text{PP}} = 285.8$  Hz, 1P) ppm. HR ESI-MS ( $m/z$ ): 702.1270 ( $[\text{M-Cl}]^+$  calc), 702.1268 (found, 20 %). IR (thin film,  $\tilde{\nu}/\text{cm}^{-1}$ ): 3270 (w), 3256 (vw), 3039 (w), 2364 (w), 2328 (w), 2001 (w), 1912 (w), 1896 (s,  $\nu_{\text{CO}}$ ), 1588 (w), 1473 (m), 1432 (w), 1420 (m), 1328 (w), 1317 (w), 1263 (w), 1152 (m), 1100 (m), 1093 (w), 1048 (w), 1004 (m), 875 (m), 737 (m), 710 (s), 663 (s), 607

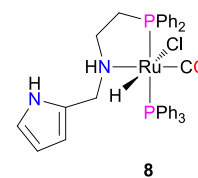
(m), 555 (w), 511 (s), 424 (m).

**Synthesis of  $[(\kappa^2\text{-L}_3)\text{Ru}(\text{H})(\text{Cl})(\text{CO})(\text{PPh}_3)]$  (**7**):** Ligand **L**<sub>3</sub> (16 mg, 0.050 mmol) and  $[(\text{PPh}_3)_3\text{Ru}(\text{H})(\text{Cl})(\text{CO})]$  (47 mg, 0.050 mmol) were dissolved in 15 mL of toluene and heated to 100 °C for 3 h, resulting in a light yellow solution. After removal of toluene, the precipitate was washed with *n*-hexane and dried under high vacuum, to give pure **7**. Single crystals suitable for single



crystal X-ray diffraction analysis were grown by layering a concentrated toluene/ $\text{CH}_2\text{Cl}_2$  solution with *n*-hexane. Yield: 34 mg (0.045 mmol, 90.1% based on Ru). Anal. Calcd. for  $\text{C}_{38}\text{H}_{36}\text{Cl}_1\text{O}_1\text{P}_2\text{Ru}_1\text{S}_1 \cdot 2.5\text{CH}_2\text{Cl}_2$  ( $M = 948.93$  g/mol) C 50.38%, N 1.45%, H 4.28%, Found: C 50.75%, N 1.19%, H 5.03%.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 25 °C)  $\delta$ : -14.48 (dd,  $^2J_{\text{PH}} = 22.6$  Hz,  $^2J_{\text{PH}} = 16.4$  Hz, 1H, Ru-H), 2.30 (m, 1H,  $\text{CH}_2$ ), 2.61 (d,  $^2J_{\text{HH}} = 12.8$  Hz, 1H,  $\text{CH}_2$ ), 2.76 (t,  $J = 11.1$  Hz, 1H,  $\text{CH}_2$ ), 2.91 (d,  $^2J_{\text{HH}} = 11.1$  Hz, 1H,  $\text{CH}_2$ ), 3.29 (m, 1H,  $\text{CH}_2$ ), 3.67 (m, 1H,  $\text{CH}_2$ ), 5.38 (br, 1H, NH), 6.22 (d,  $^3J_{\text{HH}} = 3.1$  Hz, 1H, thiophene-H), 6.80 (t,  $^3J_{\text{HH}} = 4.2$  Hz, 1H, thiophene-H), 7.11 (d,  $^3J_{\text{HH}} = 5.1$  Hz, 1H, thiophene-H), 7.33-7.51 (m, 15H,  $\text{PPh}_3$ -H), 7.67-7.88 (m, 10H,  $\text{PPh}_2$ -H) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ , 25 °C)  $\delta$ : 14.2 (s, 1C,  $\text{CH}_2$ ), 22.8 (s, 1C,  $\text{CH}_2$ ), 31.7 (s, 1C,  $\text{CH}_2$ ), 125.9 (s, 1C, thiophene-C), 127.1 (s, 1C, thiophene-C), 127.6 (s, 1C, thiophene-C), 128.6 (d,  $^3J_{\text{CP}} = 9.8$  Hz, 4C, *m*-Ph-C), 128.7 (d,  $^3J_{\text{CP}} = 9.1$  Hz, 6C, *m*-Ph-C), 129.9 (d,  $^4J_{\text{CP}} = 2.1$  Hz, 1C, *p*-Ph-C), 130.0 (d,  $^4J_{\text{CP}} = 1.1$  Hz, 3C, *p*-Ph-C), 130.3 (d,  $^4J_{\text{CP}} = 2.0$  Hz, 1C, *p*-Ph-C), 133.1 (dd,  $^1J_{\text{CP}} = 19.7$  Hz,  $^2J_{\text{CP}} = 10.9$  Hz, 4C, *o*-Ph-C), 134.3 (d,  $^2J_{\text{CP}} = 10.7$  Hz, 6C, *o*- $\text{PPh}_3$ -C), 134.9 (s, 3C, *i*-Ph-C), 135.4 (s, 2C, *i*-Ph-C), 139.3 (s, 1C, thiophene-C) ppm. The resonance corresponding to the carbonyl ligand was not observed.  $^{31}\text{P}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ , 25 °C)  $\delta$ : 43.6 (d,  $^2J_{\text{PP}} = 272.7$  Hz, 1P), 59.8 (d,  $^2J_{\text{PP}} = 284.0$  Hz, 1P) ppm. HR ESI-MS ( $m/z$ ): 718.1041 ( $[\text{M}-\text{Cl}]^+_{\text{calc}}$ ), 718.1031 (found, 25%), 456.0124 ( $[\text{M}-\text{Cl}-\text{PPh}_3]^+_{\text{calc}}$ ), 456.0132 (found, 100%). IR (thin film,  $\tilde{\nu}/\text{cm}^{-1}$ ): 3058 (vw), 2962 (w), 2898 (w), 2836 (w), 2328 (w), 1913 (m,  $\nu_{\text{CO}}$ ), 1662 (w), 1577 (w), 1556 (w), 1471 (w), 1437 (m), 1264 (m), 1099 (s), 1012 (s), 879 (w), 858 (w), 787 (s), 731 (m), 692 (vs), 594 (w), 589 (w), 502 (s), 446 (m).

**Synthesis of  $[(\kappa^2\text{-L}_4)\text{Ru}(\text{H})(\text{Cl})(\text{CO})(\text{PPh}_3)]$  (**8**):** Ligand **L**<sub>4</sub> (16 mg, 0.050 mmol) and  $[(\text{PPh}_3)_3\text{Ru}(\text{H})(\text{Cl})(\text{CO})]$  (47 mg, 0.050 mmol) in 15 mL of toluene were heated to 130 °C for 16 h, resulting in a yellow solution, after removal of solvent, the precipitate was washed with *n*-hexane. Drying at a high vacuum gave pure **8**. Single crystals suitable for single crystal X-ray diffraction analysis



were grown by layering a concentrated toluene/ $\text{CH}_2\text{Cl}_2$  solution with *n*-hexane. Yield: 17 mg (0.023 mmol, 46.1% based on Ru). Anal. Calcd. for  $\text{C}_{38}\text{H}_{37}\text{Cl}_1\text{N}_2\text{O}_1\text{P}_2\text{Ru}_1 \cdot \text{CH}_2\text{Cl}_2$  ( $M = 822.06$  g/mol) C 57.05%, N 3.41%, H 4.79%. Found: C 57.27%, N 3.38%, H 4.51%.  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_2\text{Cl}_2$ , 25 °C)  $\delta$ : -14.28 (dd,  $^2J_{\text{PH}} = 22.5$  Hz,  $^2J_{\text{PH}} = 16.0$  Hz, 1H, Ru-H), 2.28 (m, 1H,  $\text{CH}_2$ ), 2.34 (s, 3H, toluene- $\text{CH}_3$ ), 2.75 (m, 1H,  $\text{CH}_2$ ), 2.84 (d,  $^3J_{\text{HH}} = 15.1$ , 2H,  $\text{CH}_2$ ), 3.16 (br, 1H, NH), 3.40 (d,  $^3J_{\text{HH}} = 15.1$ , 1H,  $\text{CH}_2$ ), 3.55 (m, 1H,  $\text{CH}_2$ ), 5.78 (s, 1H, pyrrole-H), 5.93 (dd,  $^3J_{\text{HH}} = 5.7$  Hz,  $^3J_{\text{HH}} = 2.8$ , 1H, pyrrole-H), 6.45 (dd, 1H,  $^3J_{\text{HH}} = 4.0$  Hz,  $^3J_{\text{HH}} = 2.6$ , pyrrole-H), 6.57 (br, 1H, pyrrole-NH), 7.11-7.29 (m, 5H, toluene-H), 7.44-7.53 (m, 15H, Ph-H), 7.72-7.86 (m, 10H, Ph-H) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CD}_2\text{Cl}_2$ , 25 °C)  $\delta$ : 27.5 (s, 1C,  $\text{CH}_2$ ), 28.3 (s, 1C,  $\text{CH}_2$ ), 50.3 (s, 1C,  $\text{CH}_2$ ), 108.3 (s, 1C, pyrrole-C), 109.7 (s, 1C, pyrrole-C), 118.1 (s, 1C, pyrrole-C), 125.3 (s, 1C, *p*-toluene-C), 128.3 (d,  $^3J_{\text{CP}} = 9.8$  Hz, 4C, *m*-Ph-C), 128.7 (d,  $^3J_{\text{CP}} = 9.2$  Hz, 6C, *m*-Ph-C), 130.0 (d,  $^4J_{\text{CP}} = 1.5$  Hz, 3C, *p*-Ph-C), 130.2 (d,  $^4J_{\text{CP}} = 2.3$  Hz, 2C, *p*-Ph-C), 133.1 (d,  $^2J_{\text{CP}} = 10.7$  Hz, 4C, *o*-Ph-C), 134.6 (d,  $^2J_{\text{CP}} = 10.8$  Hz, 6C, *o*-Ph-C), 135.2 (s, 5C, *i*-Ph-C), 135.7 (s, 1C, pyrrole-C), ppm. The resonance corresponding to the carbonyl ligand was not observed.  $^{31}\text{P}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CD}_2\text{Cl}_2$ , 25 °C)  $\delta$ : 59.2 (dd,

$^2J_{PP} = 284.1$  Hz,  $J = 4.6$  Hz, 1P), 42.8 (d,  $^2J_{PP} = 286.7$  Hz, 1P) ppm. HR ESI-MS ( $m/z$ ): 699.1273 ( $[M-2H-Cl]^+_{calc}$ ), 699.1273 (found, 100%); 735.1036 ( $[M-H]^+_{calc}$ ), 735.1040 (found, 20%). IR (thin film,  $\tilde{\nu}/cm^{-1}$ ): 3069 (w), 2963 (vw), 1922 (m, CO), 1656 (w), 1497 (w), 1433 (m), 1274 (m), 1008 (s), 953 (w), 870 (w), 806 (s), 742 (m), 678 (s), 520 (s), 439 (w).

**Catalytic dehydrogenation of benzyl alcohol:** In a typical experiment pre-catalyst (5  $\mu$ mol), *m*-xylene as internal standard (106.1 mg, 1.00 mmol), benzyl alcohol (1080.6 mg, 10.00 mmol),  $KO^tBu$  (56.1 mg, 0.50 mmol) and solvent (3.00 mL) were placed in a 50 mL Schlenk-tube under nitrogen atmosphere. The mixture was heated to reflux for the specified time and the extent of conversion was frequently checked by GC-analysis using *m*-xylene as internal standard. After the reaction the mixture was chilled to ambient temperature and the yield was determined by GC analysis with *m*-Xylene as internal standard using a AGILENT GC 6850 system equipped with a HP-5 column.

**Catalytic hydrogenation of ketones:** In a typical experiment 1.00 mL of 0.50 mM solution of the pre-catalyst in  $iPrOH$  (0.50  $\mu$ mol), *m*-xylene as internal standard (106.1 mg, 1.00 mmol),  $KO^tBu$  (44.8 mg, 0.40 mmol),  $iPrOH$  (2.00 mL), ketone (5.00 mmol) were placed in a 90 mL Fischer-Porter glass autoclave under nitrogen atmosphere. The autoclave was three times charged with 3 bar of  $H_2$  and vented. The mixture was stirred under  $H_2$  (10 bar) at 60 °C for 1 h or ambient temperature for 18 h. After the specified time the mixture cooled to ambient temperature (if necessary), the pressure were carefully released and 0.100 mL of the mixture were diluted with  $iPrOH$  (3.00 mL) before analysis. The extent of conversion and the yield were determined by GC analysis with *m*-Xylene (1.00 mmol) as internal standard using a AGILENT GC 6850 system equipped with a HP-5 column. For norcamphor, the conformation of two isomer products was further determined by  $^1H$  NMR analysis.

**Catalytic hydrogenation of 3-(Dimethylamino)propiophenone hydrochloride in a biphasic water/substrate system:** 3-(dimethylamino)propiophenone hydrochloride (213.7 mg, 1.00 mmol), KOH (56.7 mg, 1.01 mmol) and degassed  $H_2O$  (3.00 mL) were placed in a 90 mL Fischer-Porter glass autoclave under nitrogen atmosphere. The mixture was stirred for 10 min in the glovebox, followed by addition of pre-catalyst (5.00  $\mu$ mol),  $iPrOH$  (0.10 mL). The autoclave was three times charged with 3 bar of  $H_2$  and vented. The mixture was stirred under  $H_2$  (10 bar) at 60 °C for 36 h. After this time the mixture was cooled to room temperature, the pressure carefully released and *m*-xylene (106.1 mg, 1.00 mmol) was added as internal standard. The mixture was three times extracted with chloroform (5 mL) and the combined extract was analyzed by gas chromatography, using a AGILENT GC 6850 system equipped with a HP-5 column. The identity of the product was further confirmed by  $^1H$  NMR spectroscopy:  $^1H$  NMR (300 MHz,  $CDCl_3$ , 25 °C)  $\delta$ : 2.12 (m, 2H,  $CH_2$ ), 2.75 (s, 6H,  $2CH_3$ ), 3.15 (m, 2H,  $CH_2$ ), 4.87 (m, 1H, CHOH), 7.24-7.42 (m, 5H, *Ph-H*) ppm, (122 MHz,  $CDCl_3$ , 25 °C)  $\delta$ : 33.7 (s, 2C,  $CH_2$ ), 43.6 (s, 2C,  $2CH_3$ ), 55.3 (s, 2C,  $CH_2$ ), 70.8 (s, 1C, CHOH), 125.3 (s, 1C, *Ph-C*), 127.1 (s, 2C, *Ph-C*), 128.6 (s, 2C, *Ph-C*), 144.0 (s, 1C, *Ph-C*).

**Catalytic hydrogenation of ketones in a biphasic water/substrate system:** In a typical experiment the ketone (5.00 mmol), the pre-catalyst (0.50  $\mu$ mol), KOH (22.4 mg, 0.40 mmol), degassed  $H_2O$  (3.00 mL) were placed in a 90 mL Fischer-Porter glass autoclave under nitrogen atmosphere. The autoclave was three times charged with 3 bar of  $H_2$  and vented. The mixture was stirred under  $H_2$  (10 bar) at 60 °C for 5 h. After this time the mixture was cooled to room temperature, the pressure carefully released and *m*-xylene (106.1 mg, 1.00 mmol) was added as



internal standard The mixture was three times extracted with chloroform (5 mL) and the combined extract was analyzed by gas chromatography, using a AGILENT GC 6850 system equipped with a HP-5 column.

## 2. NMR spectra

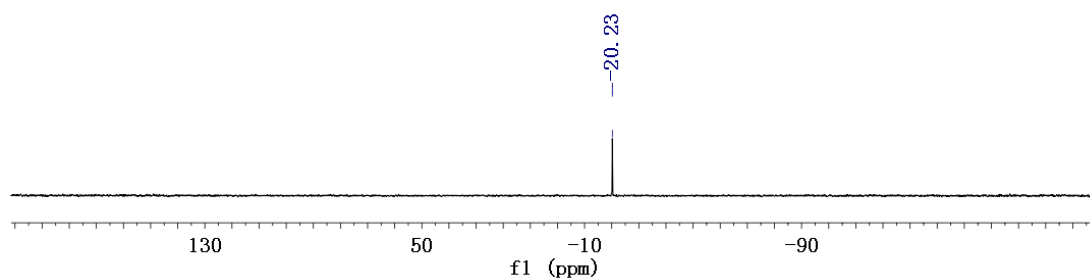


Figure S1.  $^{31}\text{P}\{^1\text{H}\}$  spectrum of  $\text{L}_1$  in  $\text{C}_6\text{D}_6$ .

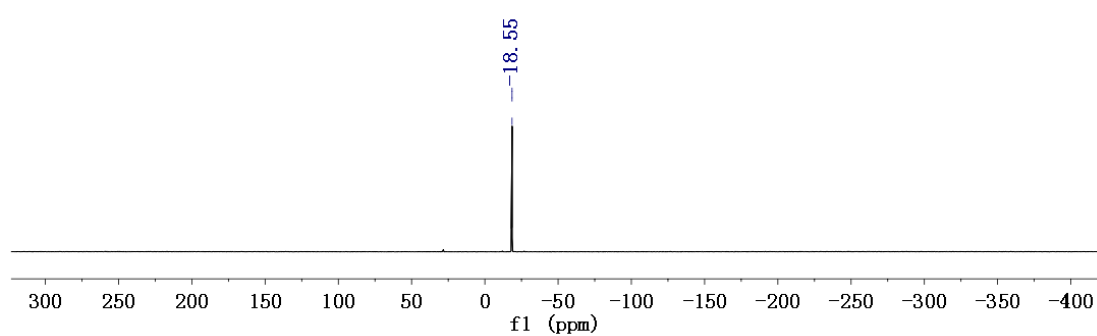


Figure S2.  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of  $\text{L}_2$  in  $\text{C}_6\text{D}_6$ .

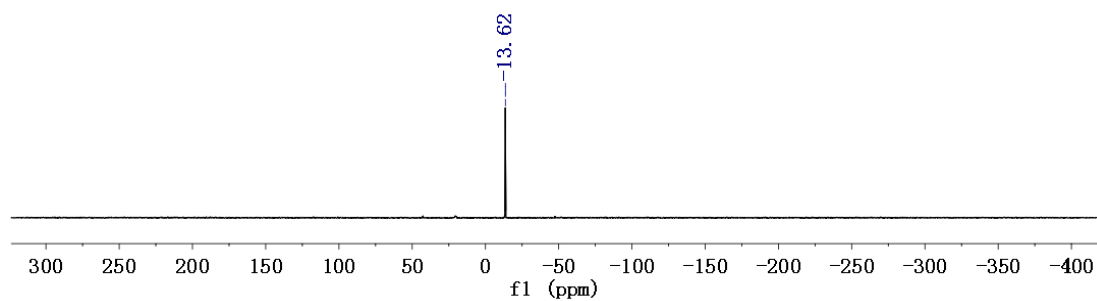


Figure S3.  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of  $\text{L}_3$  in  $\text{C}_6\text{D}_6$ .

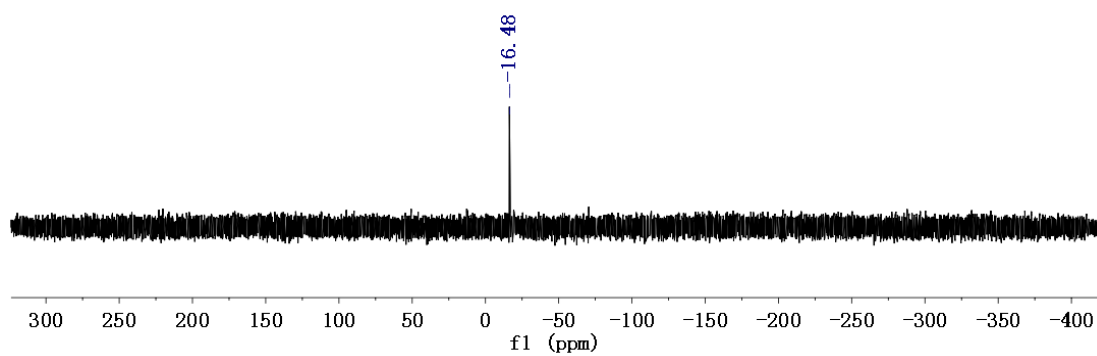


Figure S4.  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of  $\text{L}_4$  in  $\text{C}_6\text{D}_6$ .

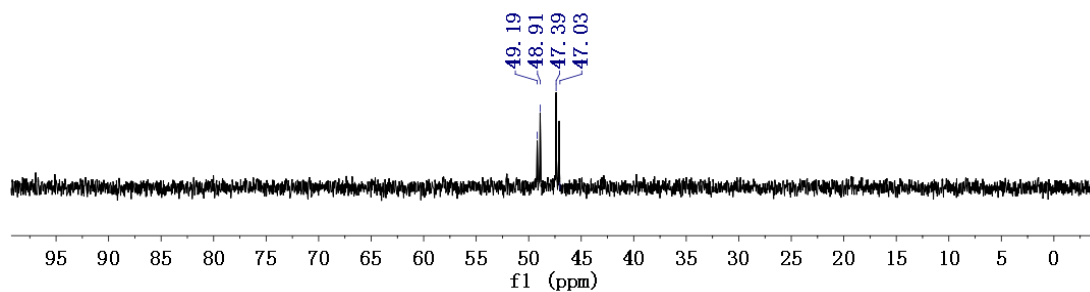


Figure S5.  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of  $[(\text{L}_1)\text{RuCl}_2(\text{PPh}_3)]$  (**1**) in  $\text{CDCl}_3$ .

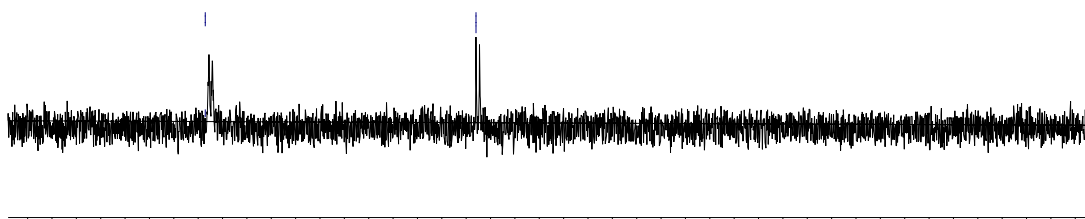


Figure S6.  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of  $[(\text{L}_2)\text{RuCl}_2(\text{PPh}_3)]$  (**2**) in  $\text{CD}_2\text{Cl}_2$ .

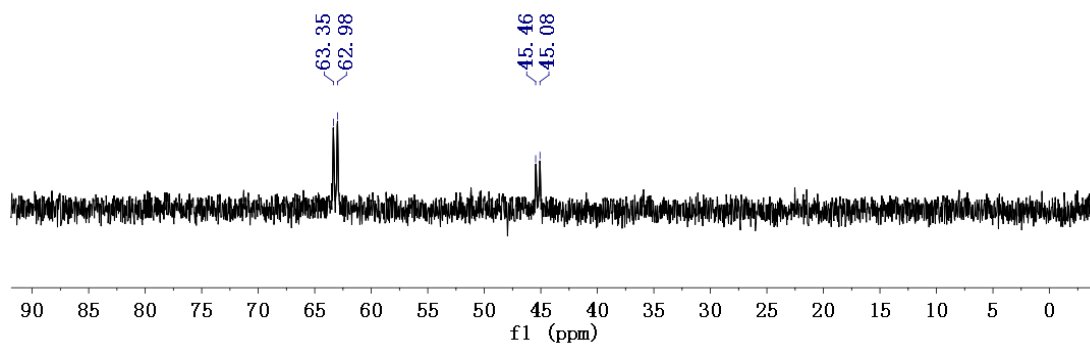


Figure S7.  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of  $[(\text{L}_3)\text{RuCl}_2(\text{PPh}_3)]$  (**3**) in  $\text{CDCl}_3$ .

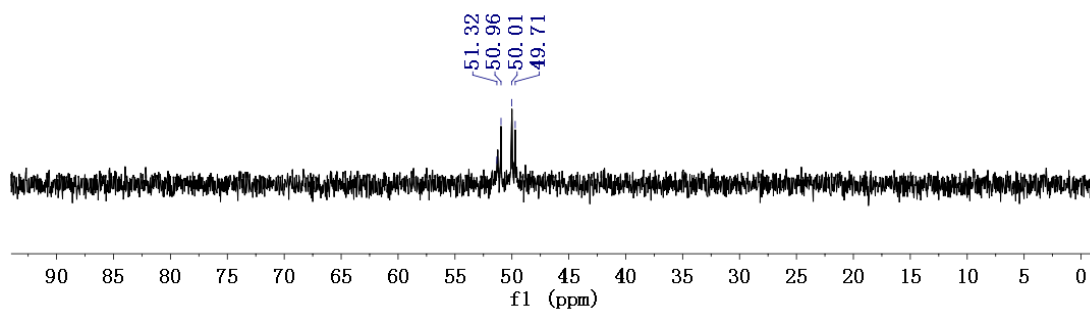


Figure S8.  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of  $[(\text{L}_4)\text{RuCl}_2(\text{PPh}_3)]$  (**4**) in  $\text{CD}_2\text{Cl}_2$ .

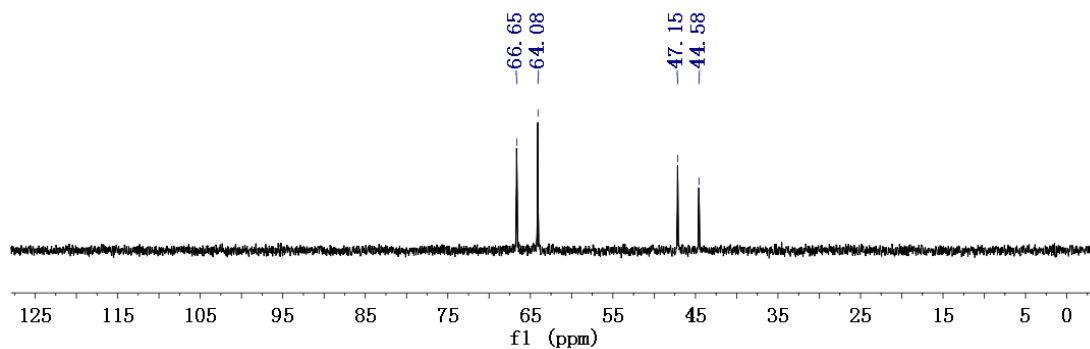


Figure S8.  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of  $[(\text{L}_1)\text{Ru}(\text{H})(\text{CO})(\text{PPh}_3)]\text{Cl}$  (**5**) in  $\text{C}_6\text{D}_6$ .

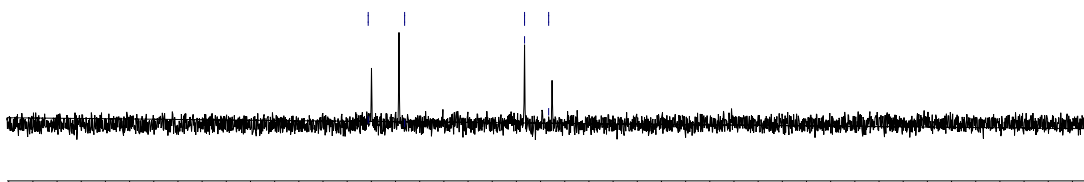


Figure S9.  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of  $[(\kappa^2\text{-L}_2)\text{Ru}(\text{H})(\text{Cl})(\text{CO})(\text{PPh}_3)]$  (**6**) in  $\text{CDCl}_3$ .

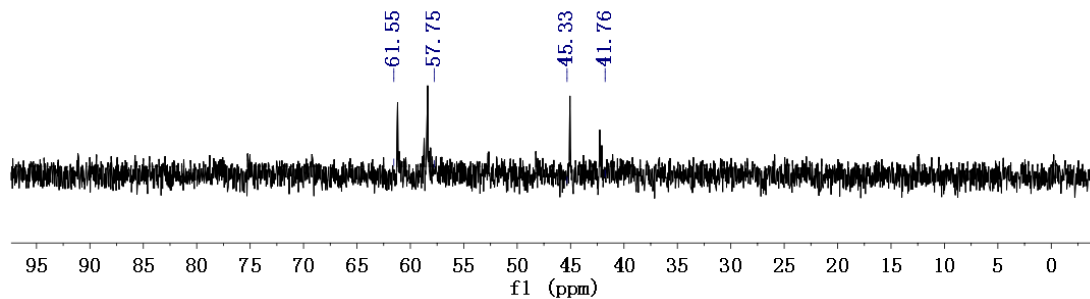


Figure S9. H, H-COSY spectrum of  $[(\kappa^2\text{-L}_3)\text{Ru}(\text{H})(\text{Cl})(\text{CO})(\text{PPh}_3)]$  (**7**) in  $\text{CDCl}_3$ .

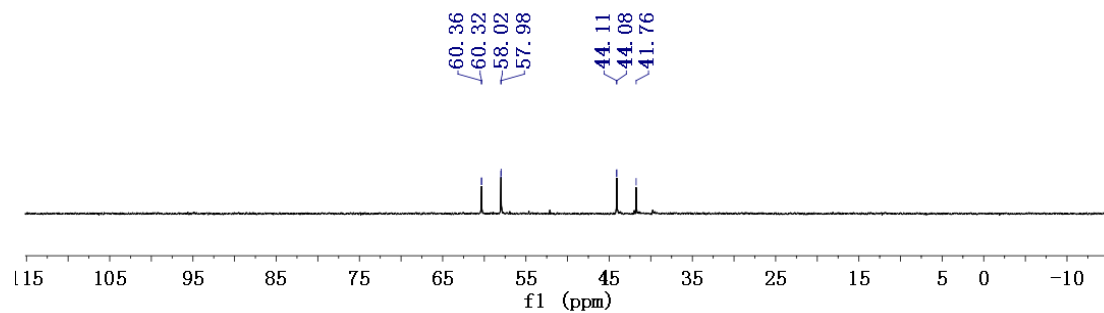
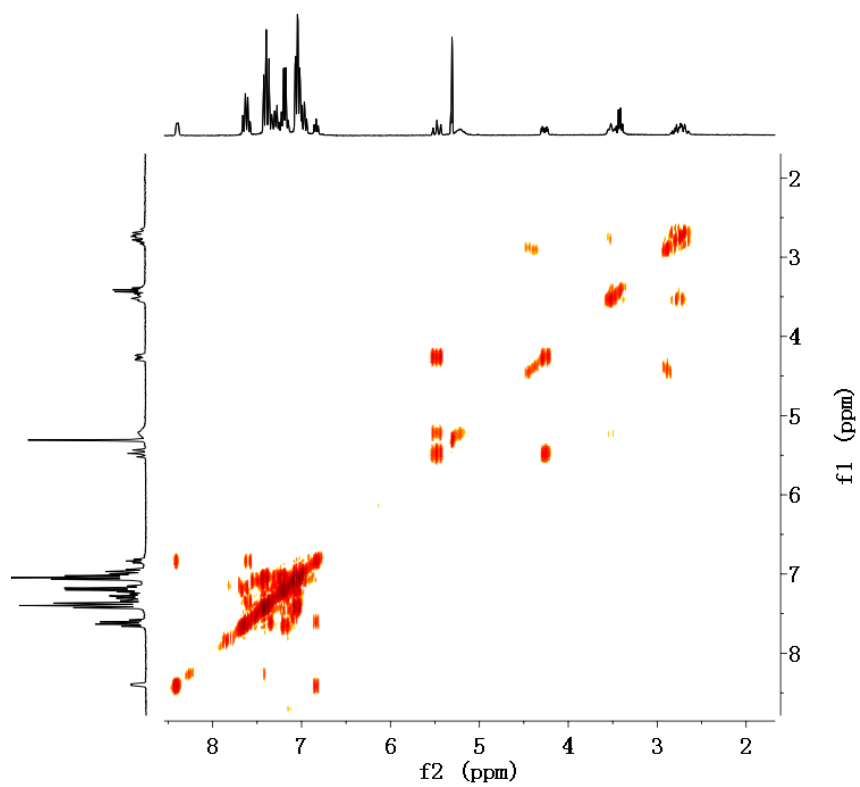
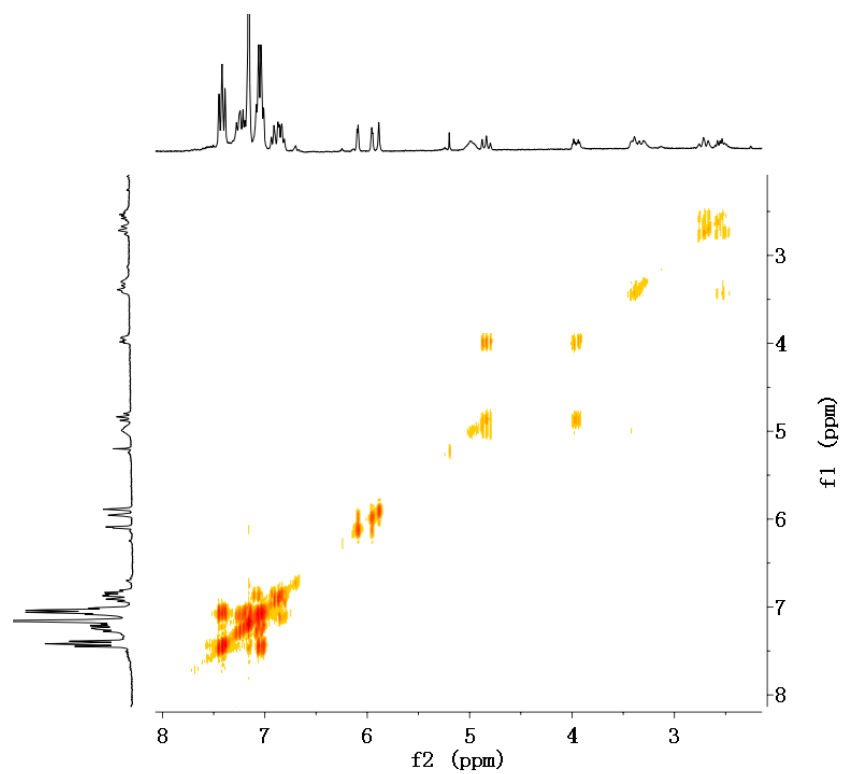


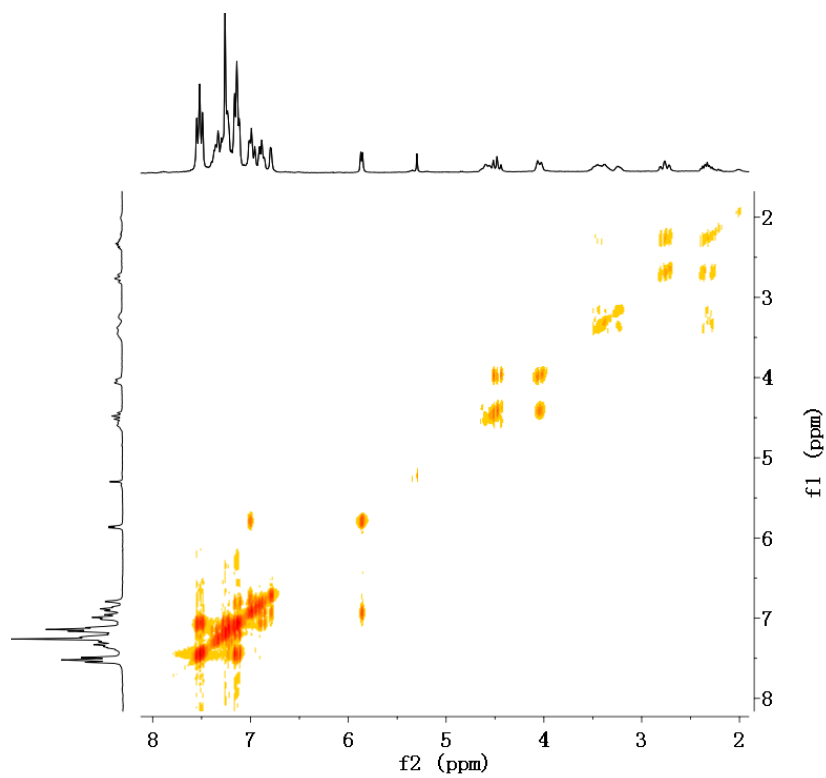
Figure S10.  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of  $[(\kappa^2\text{-L}_4)\text{Ru}(\text{H})(\text{Cl})(\text{CO})(\text{PPh}_3)]$  (**8**) in  $\text{CD}_2\text{Cl}_2$ .



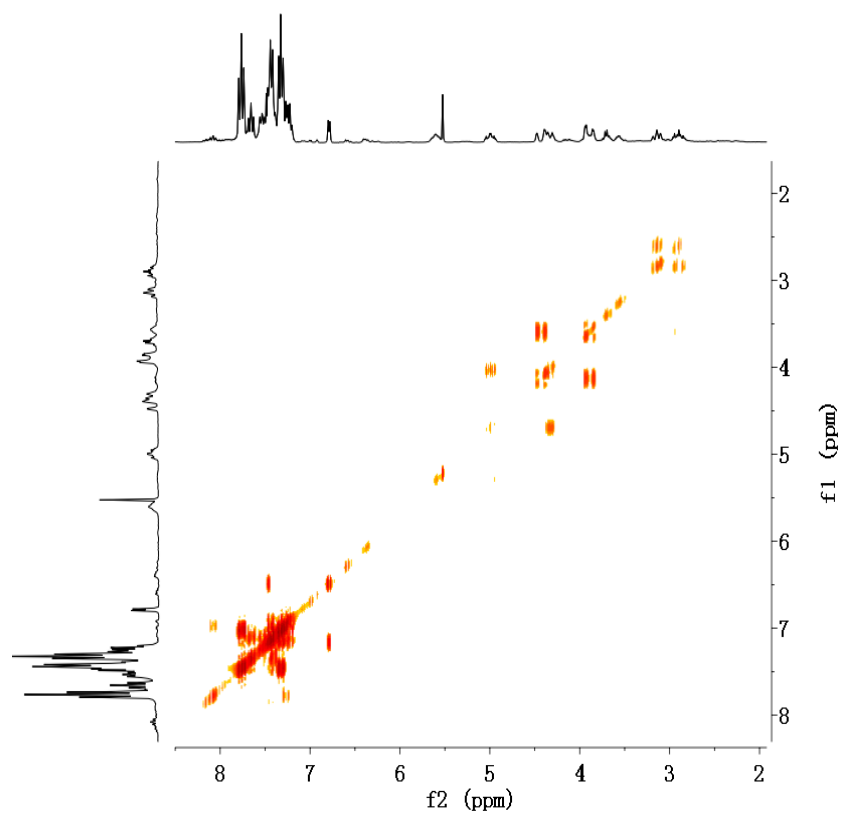
**Figure S11.**  $^1\text{H}$ -COSY NMR spectrum of  $[(L_1)\text{RuCl}_2(\text{PPh}_3)]$  (**1**) in  $\text{CDCl}_3$



**Figure S12.**  $^1\text{H}$ -COSY NMR spectrum of  $[(L_2)\text{RuCl}_2(\text{PPh}_3)]$  (**2**) in  $\text{CD}_2\text{Cl}_2$ .



**Figure S13.** <sup>1</sup>H-COSY NMR spectrum of  $[(L_3)RuCl_2(PPh_3)]$  (3) in  $CDCl_3$ .



**Figure S14.** <sup>1</sup>H-COSY NMR spectrum of  $[(L_4)RuCl_2(PPh_3)]$  (4) in  $CD_2Cl_2$ .

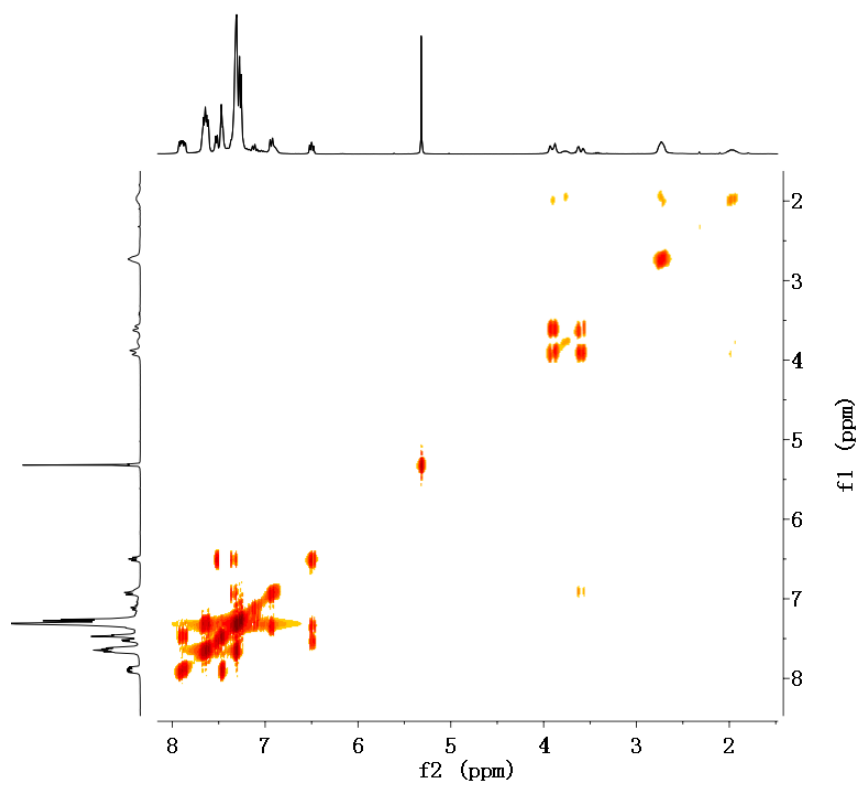


Figure S15.  $^1\text{H}$ -COSY NMR spectrum of  $[(L_1)\text{Ru}(\text{H})(\text{CO})(\text{PPh}_3)]\text{Cl}$  (**5**) in  $\text{C}_6\text{D}_6$ .

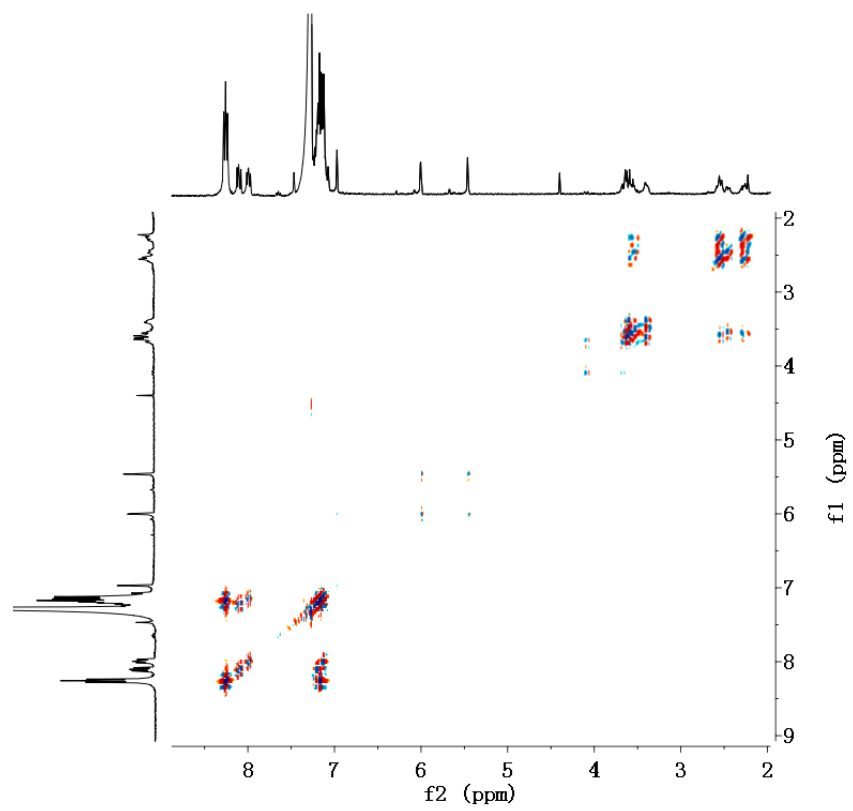
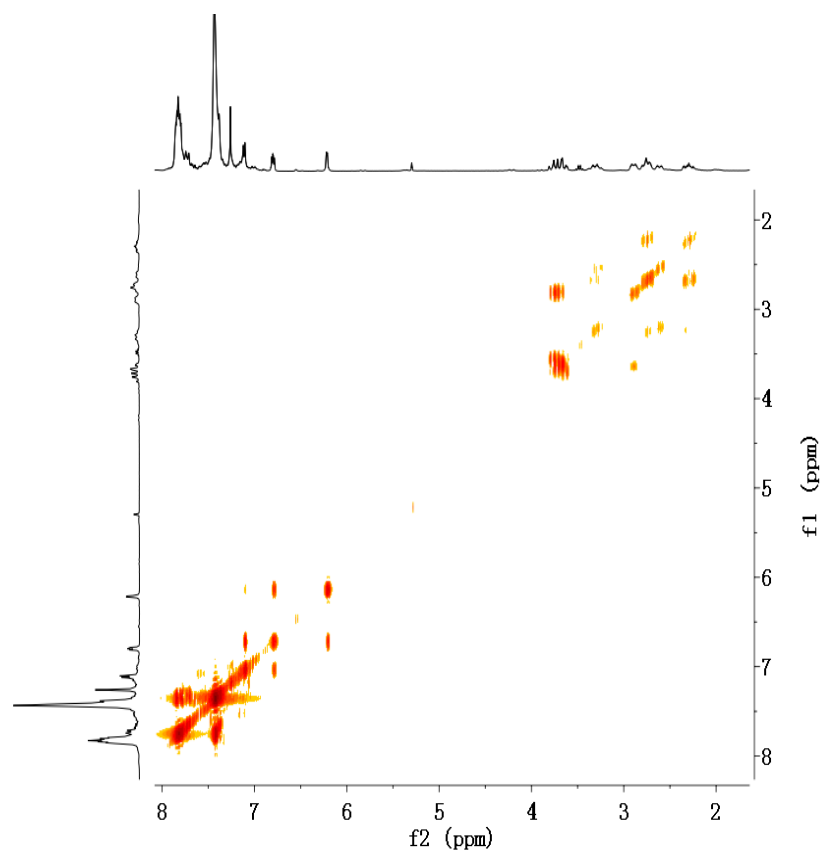
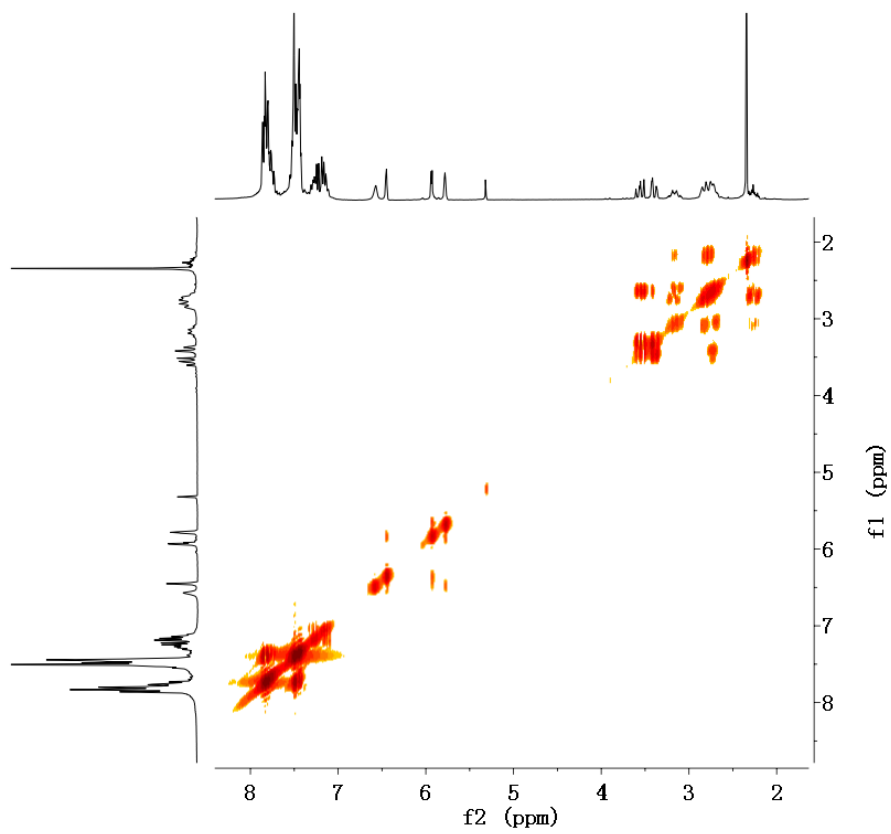


Figure S16.  $^1\text{H}$ -COSY NMR spectrum of  $[(\kappa^2\text{-}L_2)\text{Ru}(\text{H})(\text{Cl})(\text{CO})(\text{PPh}_3)]$  (**6**) in  $\text{CDCl}_3$ .



**Figure S17.** <sup>1</sup>H-COSY NMR spectrum of  $[(\kappa^2\text{-L}_3)\text{Ru}(\text{H})(\text{Cl})(\text{CO})(\text{PPh}_3)]$  (**7**) in  $\text{CDCl}_3$ .



**Figure S18.** <sup>1</sup>H-COSY NMR spectrum of  $[(\kappa^2\text{-L}_4)\text{Ru}(\text{H})(\text{Cl})(\text{CO})(\text{PPh}_3)]$  (**8**) in  $\text{CD}_2\text{Cl}_2$ .



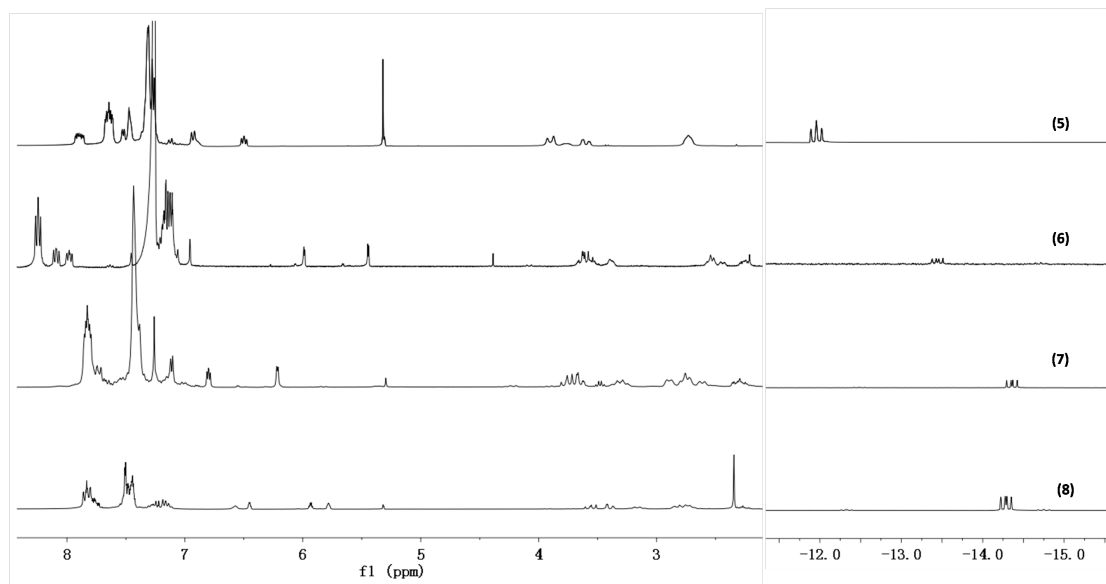


Figure S19.  $^1\text{H}$  NMR spectrum of 5-8.

### 3. X-Ray Crystallography

The single crystal X-ray diffraction data for the structural analysis has been collected using graphite-monochromated Mo-K $\alpha$ -radiation ( $\lambda_{\text{MoK}\alpha} = 0.71073 \text{ \AA}$ ) on the pixel detector system Bruker D8-Quest. The structures were solved by SHELXL-97 and refined against  $F^2$  by full-matrix-least-square techniques using SHELXL-97.<sup>4</sup> Based on the crystal descriptions, numerical absorption corrections were applied. Crystallographic data for **2-8** has been deposited at Cambridge Crystallographic Data Centre (CCDC 1401061-1401067) and can be obtained free of charge via [www.ccdc.cam.ac.uk/](http://www.ccdc.cam.ac.uk/).

**Table S1.** Crystallographic data for **2-5**.

Compound	<b>2-CH<sub>2</sub>Cl<sub>2</sub></b>	<b>3-C<sub>7</sub>H<sub>8</sub></b>	<b>4-CH<sub>2</sub>Cl<sub>2</sub></b>	<b>5-CH<sub>2</sub>Cl<sub>2</sub></b>
chemical formula	C <sub>38</sub> H <sub>37</sub> Cl <sub>4</sub> NOP <sub>2</sub> Ru	C <sub>44</sub> H <sub>43</sub> Cl <sub>2</sub> NP <sub>2</sub> RuS	C <sub>38</sub> H <sub>38</sub> Cl <sub>4</sub> N <sub>2</sub> P <sub>2</sub> Ru	C <sub>40</sub> H <sub>39</sub> Cl <sub>3</sub> N <sub>2</sub> OP <sub>2</sub> Ru
crystal color	dark red	red	dark red	yellow
Fw(g/mol)	828.50	851.76	827.51	833.09
F(000)	844	1752	844	1704
space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P2_1/n$
a (Å)	10.3466(4)	15.105(3)	10.3407(3)	16.0126(8)
b (Å)	13.6086(6)	23.880(5)	13.7742(5)	12.4920(7)
c (Å)	14.4808(6)	10.858(2)	14.2803(5)	19.8380(11)
$\alpha$ (°)	71.8190(10)	90	72.0730(10)	90
$\beta$ (°)	73.4140(10)	100.75(3)	73.1980(10)	98.418(2)
$\gamma$ (°)	73.8300(10)	90	74.1580(10)	90
Z	2	4	2	4
V (Å <sup>3</sup> )	1815.93(13)	3848.0(13)	1814.44(11)	3925.4
$\rho_{\text{calcd}}$ (g·cm <sup>-3</sup> )	1.515	1.470	1.515	1.410
$\mu$ (mm <sup>-1</sup> )	0.846	0.717	0.846	0.718
$\theta$ range (°)	4.60-56.72	4.18-52.74	4.2-56.66	4.16-54.38
completeness	0.998	1.0	0.999	0.998
collected reflections	50838	68615	25651	90045
R <sub>int</sub>	0.0322	0.1747	0.0255	0.0556
R <sub>1</sub> ; WR <sub>2</sub> [>2 $\sigma$ (I)]	0.0228, 0.0510	0.0601; 0.1081	0.0274; 0.0604	0.0389; 0.0881
R <sub>1</sub> ;WR <sub>2</sub> [all data]	0.0296, 0.0541	0.1025;0.1256	0.0358; 0.0650	0.050; 0.0934
GOF	1.047	1.116	1.0400	1.100
Max. peak/hole/eÅ <sup>-3</sup>	0.49 and -0.48	0.66/ -0.81	0.82/ -0.74	0.70 and -1.31

**Table S2.** Crystallographic data for **6-8**.

Compound	<b>6·C<sub>7</sub>H<sub>8</sub></b>	<b>7</b>	<b>8·C<sub>7</sub>H<sub>8</sub></b>
chemical formula	C <sub>45</sub> H <sub>44</sub> ClNO <sub>2</sub> P <sub>2</sub> Ru	C <sub>187</sub> H <sub>184</sub> Cl <sub>4</sub> N <sub>4</sub> O <sub>4</sub> P <sub>8</sub> Ru <sub>4</sub> S <sub>4</sub>	C <sub>45</sub> H <sub>45</sub> ClN <sub>2</sub> OP <sub>2</sub> Ru <sub>1</sub>
crystal color	yellow	yellow	yellow
Fw(g/mol)	829.27	1700	828.29
F(000)	3424.0	1794	1712
space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
a (Å)	21.311(10)	16.2877(7)	13.2654(7)
b (Å)	15.163(7)	16.7911(8)	14.1758(8)
c (Å)	26.456(12)	17.6733(9)	25.3863(14)
$\alpha$ (°)	90.00	73.121(2)	88.754(2)
$\beta$ (°)	111.72(5)	77.846(2)	80.401(2)
$\gamma$ (°)	90.00	61.9460(10)	75.564(2)
Z	8	1	4
V (Å <sup>3</sup> )	7941.9	4066.1(3)	4557.4(4)
$\rho_{\text{calcd}}$ (g·cm <sup>-3</sup> )	1.387	1.419	1.207
$\mu$ (mm <sup>-1</sup> )	0.581	0.619	0.505
$\theta$ range (°)	4.26-56.72	4.10-56.72	4.18-52.74
completeness	0.999	0.997	0.989
collected reflections	126879	174566	85841
R <sub>int</sub>	0.0798	0.0347	0.1596
R <sub>1</sub> ; WR <sub>2</sub> [I>2 $\sigma$ (I)]	0.0383;0.0866	0.0282; 0.0637	0.0807; 0.1625
R <sub>2</sub> ; WR <sub>2</sub> [all data]	0.0626;0.0965	0.0380, 0.0689	0.1551; 0.1851
GOF	1.091	1.055	1.009
Max. peak/hole/eÅ <sup>-3</sup>	0.99 and -0.66	1.19 / -0.71	0.98/ -1.08

#### 4. Literature

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